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September 11, 2002

Reference No. 19023-23

✓ KA.
9/26/02

Mr. Kevin Adler
United States Environmental Protection Agency
Region V
77 West Jackson Boulevard
Chicago, Illinois60604-3590

Dear Mr. Adler:

Re: Nitrification Study
Groundwater Pre-Design Work Plan
Waukegan Manufactured Gas and Coke Plant Site
Waukegan Illinois

We are enclosing a revised Section 3 of the Groundwater Pre-Design Work Plan. Section 3 is titled Nitrification Study Work Plan.

You may recall that the source of seed sludge that was originally proposed is no longer operational. This required an alternate acceptable source of seed sludge to be acquired. While evaluating alternative seed sludge sources several fine-tuning or optimization steps were suggested which have been incorporated into the Work Plan. In addition the groundwater sample collection has been modified to reflect groundwater quality that is expected from the groundwater Modelling results.

The changes presented do not fundamentally change the expected treatment protocols. It is expected that the changes will provide the best opportunity for biological treatment in sequencing batch reactors to be demonstrated successfully in the shortest possible time.

Please review and approve the Work Plan or contact us with any questions you may have.

Yours truly,

CONESTOGA-ROVERS & ASSOCIATES

Alan W. Van Norman

JB/pw/11
Encl.
c.c. Campbell, Jim - EMI
Keyser, Jewel - CH_2M Hill
Langseth, Jim - Barr
Matuszak, Steve - Peoples Energy
Rednour, Erin - IEPA
Smith, Phil - CH_2M Hill
Wanner, Steve - CRA

3.0 NITRIFICATION STUDY WORK PLAN

3.1 NITRIFICATION STUDY INTRODUCTION

This Nitrification Study Work Plan (NSWP) is based on the results of a Groundwater Treatability Study conducted as part of a Groundwater Pilot Project completed in 2000 to 2001 (Pilot Project Report, July 2001, CRA). The 2000 to 2001 Groundwater Treatability Study will be referred to as the Pilot Project Treatability Study in this NSWP.

During the Pilot Project Treatability Study potential technology for treating groundwater collected at the Site was evaluated in two parts; pre-treatment for arsenic removal and biological treatment for removal of organic constituents, ammonia, and thiocyanate. It was determined that Fenton's reagent treatment, a mixture of ferrous sulfate and hydrogen peroxide, can be successfully applied for removal of arsenic (generally 80 to 90 percent). During the same treatment, partial removal (approximately 15 percent) of organic contaminants and thiocyanate was also achieved.

Biological treatment of pre-treated groundwater from the Site applying sequencing batch reactor (SBR) technology removed up to 99 percent of phenols, >95 percent thiocyanate, and >90 percent of all specific organic compounds during the Pilot Project Treatability Study.

Nitrification in the SBR system was clearly established achieving up to 60 percent of ammonia removal. However, one of the conclusions of the Pilot Project Treatability Study was that the test was not planned or configured to operate long enough to fully acclimate the biomass to a very high concentration of ammonia in the groundwater (NH_3-N up to 2,000 mg/L). As a result, stable nitrification was not achieved throughout the Pilot Project Treatability Study.

The Pilot Project Report recommended that a followup bench-scale system be operated to address the following objectives:

1. longer acclimatization and operation period so that stable biological treatment is achieved;
2. parallel operation of biological treatment process with and without arsenic pre-treatment to monitor the fate of the arsenic in the process; and
3. representative influent concentrations as opposed to the startup concentrations used in the Pilot Project Treatability Study.

The purpose of this NSWP is to plan and describe a long-term operation bench-scale system that will define the parameters for successful scale up of a biological groundwater treatment system. The operation of two separate SBR reactors will be investigated. One will be fed with pre-treated groundwater while the other will be fed with non-pre-treated groundwater.

The optimized pre-treatment procedure developed in the Pilot Project Treatability study will be applied to the first SBR.

At least 100 gallons of groundwater for the treatability study will be collected from the Site and will be shipped to the CRA Treatability Laboratory. The sample will be the subject of initial tests to confirm the efficiency of the pre-treatment procedure.

The biomass used in the study will be collected from a full-scale activated sludge treatment plant that treats coke wastewater. The source is expected to be the DOFASCO Steel plant in Hamilton, Ontario, Canada.

3.2 SAMPLE COLLECTION STORAGE AND HANDLING

The Pilot Project Report demonstrated that contaminant concentrations declined significantly over the first 10 days of pumping and remained at reduced levels under the various pumping scenarios that were tested under the Pilot Project. The Pilot Project Treatability Study was conducted on groundwater from the first 2 days of pumping and, as a result, represented worst case groundwater quality. The influent concentrations to a full-scale treatment plant will be lower than those used in the Pilot Project Treatability Study as each pumping cycle will continue for many weeks.

The Pilot Project Report also demonstrated that nitrification is the process that will determine design kinetics and full-scale design parameters. Consequently, ammonia is the key parameter for determining the treatability of the Site groundwater. This Nitrification Study will be conducted with groundwater that is representative of expected long-term groundwater quality. The Pilot Project Report indicated that initial ammonia concentrations ranged from over 1,000 mg/L at the E Unit to almost 2,000 mg/L at the E/R Unit. Initial concentrations were significantly reduced after a few days of pumping to <300 mg/L at the E Unit and <200 mg/L at the E/R Unit. Preliminary Groundwater Modeling results confirm that the high initial ammonia concentrations will be significantly reduced after a few days pumping at full scale. It is not possible to predict precisely what the long-term steady state groundwater ammonia concentration will be but it will be significantly lower than the high initial ammonia

concentrations. Consequently, the Nitrification Study will be conducted on groundwater with an ammonia concentration of approximately 500 mg/L.

Preliminary modeling results also indicate that arsenic concentrations starting at 10 mg/L and dropping to 6 mg/L as well as phenols starting at 200 mg/L and dropping to 130 mg/L should be expected in some cells. As a result, the target concentrations for ammonia will be 450 to 550 mg/L, for arsenic 2.5 to 7.5 mg/L and for phenols 100 to 200 mg/L.

The E-Unit and the E/R Unit are both located close to the groundwater divide between the harbor and the lake. Consequently, it is not expected that full recovery to pre-test chemical concentrations has occurred even after 2 years of recovery. A blended sample will therefore be prepared for the Nitrification Study.

In 2001, MW-7D had 2,200 to 2,500 mg/L ammonia, 17 to 18 mg/L arsenic, and 1,500 to 1,600 mg/L phenols. EW-2 was not monitored in 2001 but is expected to have much lower concentrations of all parameters. The Nitrification Study will be conducted on a blend of water from MW-7D and EW-2. The ratio of water from each well will be adjusted to target an ammonia concentration of 500 mg/L in the blended water.

Groundwater will be collected from EW-2 and MW-7D at a rate of approximately 0.5 gallons per minute (gpm), using a peristaltic pump or pumps. The first 5 gallons pumped will be directed to a waste container. A sample will then be collected from each well. The sample will be field analyzed for pH, conductivity, temperature, oxidation/reduction potential (ORP), dissolved oxygen, and ammonia. The remaining sample will then be sent for laboratory analysis of ammonia, phenols, chemical oxygen demand, and arsenic. A 3-day turnaround will be requested.

When the laboratory results have been received, the appropriate ratio to achieve a 500 mg/L ammonia concentration will be calculated. The appropriate amounts from each well will then be pumped into a 300-gallon plastic tank. Up to twenty-five 5-gallon plastic pails will be filled from the 300-gallon tank. The 5-gallon pails will be sealed, placed in heavy plastic bags, sealed again, and packed in individual cardboard boxes for overnight shipment to the treatability laboratory.

To ensure the same groundwater quality during each study the following procedures will be applied:

1. containers will be kept at ~ 5°C and well mixed before the treatment;

2. samples for treatment will be collected in equal volumes from each of the storage containers; and

3. before treatment each batch sample (comprised of four 5-gallon pails composited into one batch) will be analyzed for the following parameters: pH, ORP, total suspended solids (TSS), turbidity, conductivity, chemical oxygen demand (COD), soluble COD (SCOD), total organic carbon(TOC), ammonia, nitrate, phosphates, cyanide, phenols, arsenic, thiocyanate, and base/neutral, and acid extractable organic compounds (the base/neutral fraction is unlikely to produce useful results and will be deleted after two analyses).

3.3 PRE-TREATMENT

3.3.1 INITIAL SCREENING TESTS

The main purpose of the screening tests is to confirm the efficiency of the pre-treatment procedure developed in the Pilot Project Treatability Study for the new groundwater sample. The dose of the chemicals will be adjusted according to the chemistry of the new groundwater sample.

The following procedures will be applied:

1. 1 liter of groundwater samples will be mixed with 1,000 mg of humates. Then 60 mg of ferrous sulfate will be added during vigorous mixing. Finally, 30 mg of hydrogen peroxide will be added and the mixture will be stirred for another 60 minutes;

2. treated samples will be analyzed for TSS, arsenic, TOC, phenols, and thiocyanate. The test will be conducted in triplicate, and the results will be averaged; and

3. if chemistry of the groundwater used in this study is substantially different from that used in Pilot Project Treatability Study (particularly regarding arsenic concentration and phenol concentration) and removal of arsenic is not satisfactory, additional tests with different doses of Fenton's reagent will be conducted.

3.3.2 BENCH-SCALE PRE-TREATMENT

Bench-scale pre-treatment will be conducted according to the procedures developed during the Pilot Project Treatability Study. The water collected at the Site will be

pre-treated in 5-gallon batches. The pre-treated water, after separating the solids by settling, will be used in one of the biological systems. The pre-treatment will be conducted at a frequency sufficient to provide supply of the influent to long-term biological treatment operation. An excess of the pre-treated water will be kept at 5°C in closed containers. As the supply of pre-treated water is depleted, freshly pre-treated water will be added to the same containers to maintain a supply of pre-treated water for use in the biological system.

Pre-treatment will be conducted in four individual 5-gallon containers during each iteration of pre-treatment. A four part composite sample of the pre-treated groundwater from each batch treatment will be analyzed for pH, TSS, VSS, COD, TOC, DOC, phenols, arsenic, ammonia, nitrate, cyanide, and thiocyanate using analytical methods presented in Table 1.

During bench scale pre-treatment, the settling time of precipitated solids and the necessity of using an organic flocculent, as was the case in the Pilot Project Treatability Study, will also be evaluated.

3.4 BIOLOGICAL TREATMENT

Biological studies will consist of the following activities:

1. acclimatization of biomass into raw and pre-treated groundwater (3 to 4 weeks); and
2. long-term operation of separate SBR reactors (3 to 4 months).

The study will be conducted in three 10-liter reactors (vessels) that will be aerated to maintain a mixed liquor D.O above 3 mg/L. The vessels will be provided with an external cold water bath and internal heaters so that the mixed liquor temperature can be controlled. Each reactor will also be provided with a pH indicator. A schematic of the batch system used in the study is presented on Figure 3.1.

3.4.1 ACCLIMATIZATION

The purpose of acclimatization is to prepare the biomass to treat the target water. Since each water stream to be treated has a specific quality, microorganisms have to modify their metabolic processes to use particular components of the groundwater as a source of food and energy.

The biomass (seed sludge) to be used in the studies will be collected from returned activated sludge at a wastewater treatment plant at the DOFASCO Steel plant in Hamilton, Ontario, Canada. This biomass is expected to be similar to the biomass that was successfully used in previous treatability studies. The biomass will be shipped to the CRA Treatability Laboratory immediately after collection in four 5-gallon plastic containers. The containers will have enough headspace to maintain aerobic conditions during shipment. The dissolve oxygen concentration will be measured several times prior to shipping the containers.

The seed sludge will be aerated for about an hour after it reaches the laboratory. A sample of the sludge will then be collected and analyzed for ammonia, nitrate and TSS.

The settling characteristics of the sludge are expected to be poor. Prior to using the sludge as seed, a set of settling tests will be performed. In these tests, the sludge will be mixed with different ratios of supernatant clear liquor from the settled sludge (or aerated tap water if necessary), and allowed to settle in 1-liter cylinders. The ratio at which the mix in a cylinder will settle to a clear volume between 250 to 375 ml in 30 minutes should be considered as the mix to be used in the reactor to start the acclimatization study.

The following acclimatization procedure will be followed in the laboratory.

Initially, approximately 5 liters of the seed sludge mixed with water in the ratio determined from the settling test will be placed in each of three reactors SBR-1, SBR-2, and SBR-3 and aerated for 1 day. During this aeration period, the temperature of the mixed liquor will be maintained at about 80°F and pH maintained at about 7.3 (between 7.0 and 8.5). Samples of the biomass will also be examined under the microscope every few hours to confirm the vitality of the microorganisms.

At the end of the 1-day aeration period, a sample of the mixed liquor should be analyzed for ammonia with a quick test kit. A second sample will be analyzed for ammonia, nitrate, and TSS at an analytical laboratory.

The two reactors (SBR-1 and SBR-2) will be fed with groundwater (raw and pre-treated, respectively), while the third reactor (SBR-3) will be used as a back up source of biomass in the case of any unexpected problems in operation of reactors SBR-1 or SBR-2.

The biomass in the reactor SBR-3 will be aerated and maintained at a pH of about 7.3 and at a temperature of 80°F . Soda Ash solution and phosphoric acid will be used for

the pH adjustment in these reactors. Phosphoric acid will also be added to provide the biomass with nutrient. Initially, about 10 ml of ground water will be added to this reactor, which should slowly be increased (about 15 percent each day) to 200 ml over a period of 2 to 3 weeks to maintain a sufficient concentration of the nitrifiers. The biomass from reactor SBR-3 will be used to supplement the biomass in SBR-1 or SBR-2, only when nitrification in SBR-1 or SBR–2 is totally upset.

The aeration in SBR-3 will cause evaporation. The loss in evaporation in this reactor will be adjusted by adding aerated tap water periodically (i.e., chlorine free).

On the first day, the reactors SBR-1 and SBR-2 will be fed with a small volume (approximately 500 ml) of raw (SBR-1) or pre-treated (SBR-2) groundwater while maintaining a mixed liquor temperature of 80°F and pH at the desired range. The pH, temperature, and DO of each treatment reactor will be recorded at least 3 times per day. The feed addition during the acclimatization period will be done while aeration continues. After groundwater addition, samples from both reactors will be collected and analyzed for pH, TSS, VSS, phenols, COD, SCOD, ammonia, and nitrate. After 1 day of aeration, samples will be collected and analyzed (by test kit) for ammonia only. If results of analyses indicate that the ammonia in the mixed liquor is close to 3 mg/L groundwater, then the groundwater addition rate will be increased by 15 percent.

At the end of a 24-hour period, if the residual ammonia in the mixed liquor in any of the reactors is over 3 mg/L, aeration will be continued for another 24-hour period. The groundwater feed will resume only when the ammonia concentration in the mixed liquor is down to about 3 mg/L (by quick test kit). A 15 percent increase in the groundwater feed will resume when the biomass in the reactor achieves a nitrification rate lowering the ammonia in the mixed liquor to about 3 mg/L in 24 hours. Samples of supernatant from both reactors will be collected daily and analyzed (by test kit) for ammonia and by a laboratory method for TSS and Nitrate Daily samples of the biomass will also be collected and examined under the microscope to assess the vitality and diversity of the microorganisms. Samples of supernatant from both reactors will be collected weekly and analyzed for ammonia, nitrate, SCN, TSS, VSS, COD, SCOD.

No biomass will be intentionally wasted during acclimatization [unless excessive growth of mixed liquor volatile suspended solids (MLVSS) occurs]. However, the operating SRT of the system during this acclimatization period will be calculated and recorded, based on solids leaving the system with the effluent and with the samples withdrawn.

The following, therefore, summarizes the acclimatization period activities:

- SBR-1 and SBR-2 will be filled up to the full operating volume using the recycled seed sludge mixed with aerated tap water to achieve desired settling.
- The reactors will be aerated to maintain a mixed liquor D.O > 3 mg/L.
- The mixed liquor temperature will always be maintained at about 80°F, pH between 7.0 and 8.5, a dissolved oxygen concentration above 3 mg/L.
- Phosphoric acid should be added to provide the biomass with desired nutrient supply.
- The reactors are expected to experience significant evaporation throughout the study. It may be necessary to make up the volume lost by evaporation by adding aerated tap water.
- The acclimatization will start adding 500 ml of groundwater to each of the reactors with air on.
- The feed rate to the reactors will not be increased till the biomass in the reactor nitrifies ammonia in the feed to about 3 mg/L in 24 hours.
- The feed rate to the reactors will be increased at a rate not exceeding 15 percent in 24 hours when the reactors will degrade ammonia in the feed to below 3 mg/L in 24 hours.
- Ammonia in the mixed liquor will be checked by quick test kit first thing every morning after ensuring the reactors maintained the desired pH, temperature, and D.O level.
- The decision to continue aeration or increase the feed will be made based on the quick test kit results.
- The ammonia concentration in the mixed liquor will again be checked and noted in the afternoon.
- Acclimatization of the biomass in a reactor will be completed when the treatment system will demonstrate 7 days of steady nitrification at a feed rate achieving desired 3 days HRT.
- Microscopic examination of the biomass should indicate diversity and vitality of microorganisms.

It is possible that 3 days HRT may not achieve steady nitrification. If it is found that the system fails to achieve total ammonia removal at a certain HRT for 7 days in a row, the HRT at which the system achieves steady nitrification should be used as a starting point for the long term study.

- The sampling and analysis of the samples to be collected and analyzed have been presented earlier.

3.4.2 LONG-TERM BIOLOGICAL TREATMENT

The purpose of the long-term biological treatment is to determine the optimum lengths of various stages of the treatment cycle and identification of any problems related to accumulation of inhibitory substances in the biomass. It is also expected that parallel operation of two biological systems, one fed with raw groundwater while the other fed with pre-treated water will provide useful information for the design of a full-scale treatment system, as well as estimation of capital and operational costs.

To facilitate comparison of the two treatment systems, the same treatment strategy will initially be applied to SBR-1 and SBR-2.

The initial strategy for both reactors will be:

Hydraulic Retention Time (HRT):	~3 days
Solid Retention Time (SRT):	~100 days
Mix Liquor Suspended Solids (MLSS):	~5,000 mg/L

The SRT will be reduced as much as possible after a vigorous biological mass is established but will not be reduced below 50 days.

Operational parameters:

At the conclusion of the acclimatization period, the reactor fill cycle will be increased to two cycles per day for a few days. The reactor fill cycle will then be increased to three fill cycles per day. During this period of operation, the groundwater feed will be added with the air supply off. The time schedule for each cycle is summarized as follows:

	2-Cycle/Day	*3-Cycle/Day*
Non aerated/mixed fill	3 hours	2 hours
Aerated react	5.5 hours	3 hours
Settle	2.5 hours	2 hours
Draw	1 hour	1 hour
Dissolved oxygen	>5 mg/L	>5 mg/L
pH	7 to 8	7 to 8

After approximately 1 month of operation, hydraulic retention time (HRT) will be gradually reduced to the value that still allows for stable nitrification. It is expected that the final HRT for reactor SBR-1 will be longer than that for SBR-2. It is also expected that it will take approximately 1 week to determine the minimum HRT, and that some adjustment to operational parameters will be necessary to optimize treatment. An application of organic polymers to improve solids settling and improve quality of the effluent will also be investigated in both biological treatment systems. As these organics polymers are biodegradable, they will be added (if needed) just 15 minutes before the air is shut off to the system for settling.

After both systems have produced good quality effluent for 1 month and the HRT has been minimized, a detailed evaluation of each of the treatment systems will be conducted. During the evaluation, both systems will be operated for three HRT cycles. After each HRT cycle, samples will be collected and analyzed for TSS, VSS, ammonia, nitrate, COD, SCOD, TOC, DOC, arsenic, phenols, and thiocyanate. During this period of operation wasted sludge will be saved and composited to make up two samples of sludge for sludge disposal characterization.

When minimum HRTs for SBR-1 and SBR-2 are determined, the impact of various operational parameters (e.g., duration of fill, react and settle periods, temperature) on effluent quality will be investigated. Two iterations for each of fill time, react time, and settling period will be conducted. Each iteration will be operated for three HRT. The temperature will be reduced during the final run.

Samples of the effluent from both reactors will be collected daily, and analyzed for ammonia by quick test kit. The collected samples will be composited and analyzed for TSS, VSS, COD, DOC, phenols, ammonia, and nitrate once a week. A composite of daily samples will be collected over a period of a few days to a maximum of 1 week, and will be analyzed for arsenic, thiocyanate.

An excess of biomass from both reactors will be wasted regularly to maintain the target SRT. Collected biological sludges will be composited and analyzed for arsenic once a week to investigate the accumulation of this metal.

After operational parameters are determined and in order to investigate any inhibitory effects on nitrification that may be the result of accumulation of metals and organic substances in the biomass, the reactors will be run at optimum operating parameters for at least one sludge retention time (SRT), or 60 days, whichever is lower. After three HRT of optimized operation, the temperature will be reduced from 80°F to room temperature (approximately 72°F). After six HRT, the temperature will be reduced to 60°F for the

balance of the run. Minor modifications to operating variables may be made to optimize operation at lower temperatures.

3.5 REPORTING

A report generated from the treatability study will consist of the following elements:

- detailed testing procedures including sampling and analyses;
- description of equipment used during the study;
- summary of data from pre-treatment including tables and graphs demonstrating the effect of Fenton's reagent composition and concentration on the removal of arsenic, COD, thiocyanate, and phenols;
- analyses of data from biological treatment of the water that will identify the operational parameters affecting removal of organic substances, thiocyanate, and ammonia;
- summary of data from the whole treatment system that will allow optimization of the full-scale treatment plant; and
- evaluation of the potential impact of re-injection of the effluent from the treatment plant into the aquifer on the groundwater quality.

TREATMENT ASSESSMENT AND DATA ANALYSIS

Based on treatability studies results it is expected that the following goals will be accomplished:

1. determination of nitrification efficiency for raw and pre-treated groundwater; this will allow for evaluation of the necessity of groundwater pre-treatment;
2. determination of arsenic fate during biological treatment and the impact of accumulation of arsenic in the biomass during nitrification, analyses of the biomass for arsenic will also allow to determine if this phenomenon makes wasted sludge a hazardous wastes which would affect disposal; and
3. treatment process design, treatability data will allow to design the full-scale process and estimate the sizes of specific treatment units and sludge generation rates.

3.6 TREATABILITY STUDY SCHEDULE

After arrival of the groundwater and activated sludge samples at the CRA Treatability Laboratory the following activities will be implemented:

Week 1

i) Sample collection.

Week 2

i) Confirmation of Fenton's reagent treatment as described in Section 3.3.1

ii) Obtain activated sludge and characterize.

iii) Setup of biological treatment systems.

Weeks 3 to 6

i) Bench-scale pre-treatment of the groundwater using procedure described in Section 3.3.2.

ii) Acclimatization of the activated sludge in reactors SBR-1, SBR-2, and SBR-3, according to the procedure described in Section 3.4.1.

Weeks 7 to 10

i) Startup of two initial biological treatment trains using acclimatized activated sludge with and without pre-treated water.

ii) Monitoring of the treatment system according to the procedure described in Section 3.4.2.

iii) TCLP test with solids generated during biological treatment of the groundwater without pre-treatment.

Weeks 11 to 27

i) Long-term biological treatment according to the procedure described in Section 3.4.2.

Weeks 28 to 31

Data compilation and evaluation of treatment as described in Section 5.0.

TABLE 1

LIST OF ANALYTICAL METHODS
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
WAUKEGAN, ILLINOIS

Parameter	*Matrix*	*Method*
Total Phenolics	Water	EPA 420.2
Arsenic	Water	SW-846 6010B
Ammonia	Water	EPA 350.1
VOCs	Water	SW-846 8260B
SVOCs	Water	SW-846 8270C
Nitrate	Water	EPA 353.4
COD/SCOD	Water	EPA 410.4
TOC/DOC	Water	SM 5310B
Cyanide	Water	EPA 335.4
Thiocyanate	Water	SM 4500-CN M
TSS	Water	EPA 160.2
VSS	Water	EPA 160.3
pH	Water	EPA 150.1
Turbidity	Water	SM 2130B
Conductivity	Water	SM 2510B
ORP	Water	Meter
Phosphate	Water	SM 4500-P
DO	Water	SM 4500-0

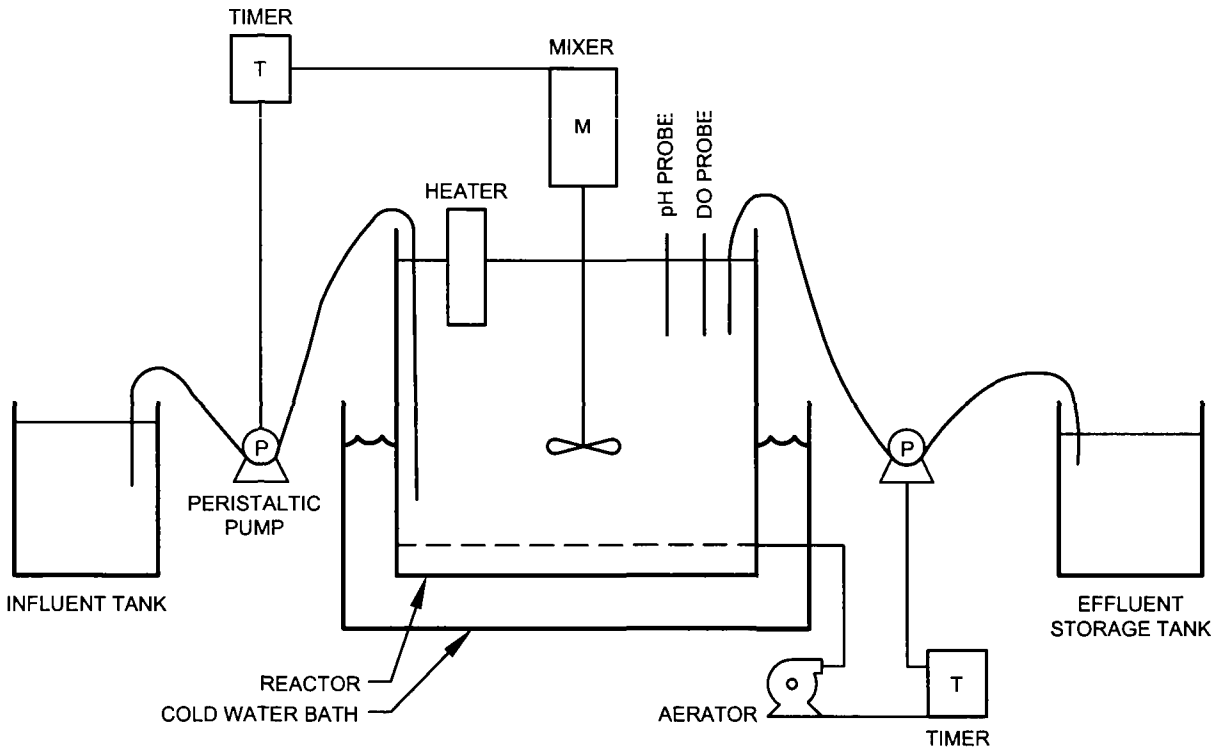

figure 3.1

BATCH TREATMENT SYSTEM SCHEMATIC
NITRIFICATION STUDY
WAUKEGAN MANUFACTURED GAS AND COKE PLANT SITE
Waukegan, Illinois